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(54) Method for producing isocyanatoalkyl (meth)acrylate

(57) A method for producing an isocyanatoalkyl (meth)acrylate substantially free of hydrolyzable chloride, comprising adding an amine and/or an imidazole and an epoxy group-containing compound and then purifying by distillation the isocyanatoalkyl (meth)acrylate until a 2-chloropropionic acid isocyanatoalkyl ester of an isocyanatoalkyl acrylate or a 2-methyl-2-chloropropionic acid isocyanatoalkyl ester of an isocyanatoalkyl methacrylate is substantially eliminated.

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to an isocyanatoalkyl (meth)acrylate substantially free of hydrolyzable chloride, which is obtained by removing hydrolyzable chloride from an isocyanatoalkyl (meth)acrylate containing hydrolyzable chloride, and a production method therefor. The isocyanatoalkyl (meth)acrylate substantially free of hydrolyzable chloride provided by the present invention is useful particularly as a material or raw material of a photoresist and the like for electronic materials.

[0002] In the present invention, unless otherwise indicated, the term "(met)acrylate" includes acrylate and methacrylate.

2. Description of Related Art

[0003] The isocyanatoalkyl (meth)acrylate represented by 2-isocyanatoethyl methacrylate is a compound containing both an isocyanato group highly reactive with a compound having an active hydrogen, for example, a compound having a substituent such as a hydroxyl group or a primary or secondary amino group and a vinyl polymerizable carbon-carbon double bond within the same molecule. This is an industrially very useful compound and it is used in many applications such as paints, coating materials, adhesives, photoresists, dental materials and magnetic recording materials. This compound is produced using phosgene as described in U.S. Patent No. 2,821,544 and Japanese Unexamined Patent Publication No. 54-5921 (JP-A-54-5921) and in general, contains an impurity called "hydrolyzable chloride". In the present invention, unless otherwise indicated, the term "hydrolyzable chloride" means chlorine in a chlorine-containing compound which is hydrolyzable. A representative example of the compound is a chlorine-containing compound such as (meth)acryloyloxyalkylcarbamoyl chloride present in a product containing the desired object in the production of an isocyanatoalkyl (meth)acrylate.

[0004] If a urethane acrylate or the like is produced using an isocyanatoalkyl (meth)acrylate containing a hydrolyzable chloride, the hydrolyzable chloride acts as a catalyst poison. Moreover, the chlorine compound mixed with a product adversely affects weatherability and corrosion resistance. In particular, the presence of hydrolyzable chloride may be fatal to the photoresist material for electronic equipment use.

[0005] Heretofore, various methods for reducing the hydrolyzable chloride in an isocyanato compound in general have been disclosed.

[0006] For example, Japanese Unexamined Patent Publication No. 53-119823 (JP-A-53-119823) discloses a method of mixing a hydrolyzable chloride-containing isocyanato compound with a fine alkali metal carbonate at a high temperature for a long period of time. Japanese Unexamined Patent Publication No. 59-172450 (JP-A-59-172450) discloses a method of adding a carboxylate of zinc and a hindered phenol-type antioxidant to a hydrolyzable chloride-containing isocyanato compound and subjecting the mixture to heat treatment and then distillation. U.S. Patent No. 3,465,023 discloses a method of synthesizing an isocyanate in a water-insoluble solvent and then rinsing it with an aqueous sodium hydrogen carbonate solution; and German Patent No. 2,249,375 discloses a method of treating a hydrolyzable chloride-containing polymethylenepolyphenyl isocyanate with an epoxy compound.

[0007] Furthermore, as a method which does not use chemicals such as an alkali metal carbonate described above, Japanese Unexamined Patent Publication No. 61-161250 (JP-A-61-161250) discloses a method of vaporizing a hydrolyzable chloride-containing isocyanato compound and then purifying the isocyanato compound by condensation at a temperature of 70°C or higher.

[0008] However, these methods cannot achieve satisfactory reduction of hydrolyzable chloride or have various problems to be solved in their industrial implementation. For example, according to the method of mixing a hydrolyzable chloride-containing isocyanato compound with an alkali metal carbonate at a high temperature described in Japanese Unexamined Patent publication No. 53-119823, the isocyanato compound and the carbonate after treatment are difficult to separate, which gives rise to inevitable generation of loss. The method involving rinsing with an aqueous sodium hydrogen carbonate solution described in U.S. Patent No. 3,465,023 is disadvantageous in that white insoluble matters precipitate at the boundary between an organic phase and an aqueous phase and this renders the subsequent separation operation cumbersome or causes contamination of the apparatus. Furthermore, these methods have the concern that isocyanato compound is contaminated with sodium ion. Even if the sodium ion content is on the order of ppm, a serious problem arises in using the isocyanato compound in electronic materials.

[0009] Particularly, in purifying an isocyanato compound having a carbon-carbon double bond, the hydrolyzable chloride content must be effectively reduced while preventing a polymerization reaction between the isocyanato compounds with each other. However, satisfactory results cannot be achieved by the above-described methods.

[0010] U.S. Patent No. 4,310,688 discloses a method of treating a methylene chloride solution of isocyanatoethyl methacrylate containing 0.21% of hydrolyzable chloride with a vicinal epoxy group-containing compound such as 1,2-butylene oxide to thereby reduce the hydrolyzable chloride content to 0.05%. However, by this method, the hydrolyzable chloride content can be reduced at most only to hundreds of ppm and the purified isocyanato compound obtained does not have sufficient properties for use in electronic materials.

[0011] In order to solve these problems in conventional techniques, the present inventors have proposed a method of reducing the hydrolyzable chloride content in an isocyanato compound by treating it with an epoxy compound in the presence of an amine, as described in Japanese Unexamined Patent Publication No. 9-323958 (JP-A-9-323958). This method is an excellent method but still fails to achieve complete removal of hydrolyzable chloride.

[0012] On the other hand, a method of producing an isocyanato compound without using phosgene has also been studied. For isocyanatoalkyl (meth)acrylate, a method using thermal decomposition of a urethane compound has been proposed (see, U.S. Patent No. 2,718,516, Japanese Unexamined Patent Publication Nos. 62-10053 (JP-A-62-10053), 62-195354 (JP-A-62-195354), 5-186414 (JP-A-5-186414), 5-186415 (JP-A-5-186415) and 6-263712 (JP-A-6-263712)). This method comprises a step of thermal decomposition at a high temperature and since the isocyanatoalkyl (meth)acrylate is very readily polymerized, the yield is not satisfactory by any means in view of profitability.

SUMMARY OF THE INVENTION

[0013] The present invention has been made to solve the problems in conventional techniques.

[0014] An object of the present invention is to provide a method for industrially producing an isocyanatoalkyl (meth) acrylate substantially free of hydrolyzable chloride from an isocyanatoalkyl (meth)acrylate produced using phosgene.

[0015] As a result of extensive investigations to attain the above-described object, the present inventors have accomplished the present invention.

[0016] More specifically, the present invention provides the following embodiments.

(1) a method for producing an isocyanatoalkyl (meth)acrylate substantially free of hydrolyzable chloride, comprising purifying an isocyanatoalkyl (meth)acrylate containing a hydrolyzable chloride until a 2-chloropropionic acid isocyanatoalkyl ester of an isocyanatoalkyl acrylate or a 2-methyl-2-chloropropionic acid isocyanatoalkyl ester of an isocyanatoalkyl methacrylate is substantially eliminated;

(2) the production method as described in (1) above, wherein the isocyanatoalkyl (meth)acrylate used in the purification step has a hydrolyzable chloride content of 100 ppm or less;

(3) the production method as described (2) above, wherein the isocyanatoalkyl (meth)acrylate containing a hydrolyzable chloride is treated with an epoxy group-containing compound and an amine and/or an imidazole to reduce the content of the hydrolyzable chloride in the isocyanatoalkyl (meth)acrylate to 100 ppm or less, and then further purified;

(4) the production method as described in (1) to (3) above, wherein the purification is performed by distillation at a distillation temperature of less than 100°C under reduced pressure in the presence of a polymerization inhibitor;

(5) the production method as described in (3) or (4) above, wherein the amine is a trialkylamine (with the alkyl group having from 4 to 15 carbon atoms) or a compound represented by the following formula (I)

$$H_2N\text{-}(CH_2CH_2NH)_n\text{-}H \qquad (I)$$

wherein n represents an integer of 2 or more, and the imidazole is a 2-alkyl-4-alkylimidazole with the alkyl groups each independently having from 1 to 3 carbon atoms;

(6) the production method as described in (3) to (5) above, wherein the treatment is performed using an epoxy group-containing compound in an amount of from 1 to 10 molar times and an amine and/or an imidazole in an amount of from 0.2 to 2 molar times the content of the hydrolyzable chloride;

(7) the production method as described in (1) to (6) above, wherein the isocyanatoalkyl (meth)acrylate is 2-isocyanatoethyl methacrylate;

(8) an isocyanatoalkyl (meth)acrylate substantially free of hydrolyzable chloride, comprising the isocyanatoalkyl acrylate containing substantially no 2-chloropropionic acid isocyanatoalkyl ester or the isocyanatoalkyl methacrylate containing substantially no 2-methyl-2-chloropropionic acid isocyanatoalkyl ester; and

(9) 2-isocyanatoethyl methacrylate substantially free of hydrolyzable chloride, which contains substantially no 2-methyl-2-chloropropionic acid 2-isocyanatoethyl ester.

ysis of hydrolyzable chloride and seems to have no relation, however, by removing these, an isocyanatoalkyl (meth) acrylate substantially free of hydrolyzable chloride can be obtained.

[0042] Although depending on the kind of the compound, the following detection conditions of gas chromatography are usually employed in case of 2-isocyanatoethyl methacrylate as a representative example.

Column	DB-1, manufactured by J&W Scientific inner diameter: 0.32 mm, length: 30 m, liquid phase film thickness: 1.0 μm
Temperature	
column	80°C for an initial 8 minutes, then the temperature is elevated at 10°C/min, and the final temperature is 300°C.
injector	200 to 300°C
detector	300°C
Detector	flame ionization detector
Carrier gas	helium
flow rate	column: 3 ml/min, split: 100 ml/min.

[0043] The present invention is described in greater detail below by referring to the Examples, however, the present invention is by no means limited to these Examples. Unless otherwise indicated, all parts, percentages and the like are by weight.

Example 1

[0044] To a 500 ml-volume glass-made reactor equipped with a distilling head (reflux ratio regulating), a thermometer, a stirrer and a heating bath, 300 g of 2-isocyanatoethyl methacrylate (boiling point: 211°C) having a hydrolyzable chloride content of 381 ppm, 1.7 g of an epoxidated fat and oil-type plasticizer (molecular weight: about 1,000, iodine value: 7) having an oxirane oxygen content of 6.1%, 0.3 g of 2,6-di-tert-butyl-4-methylphenol and 0.11 g of triethylene-tetramine (boiling point: 277.4°C) were charged. The mixture was stirred at 60°C for 2.5 hours and then distilled at about 1.3 kPa and 85°C. After the initial fraction reached 10% of the charge, the receiver was changed. Then, 220 g of purified 2-isocyanatoethyl methacrylate was obtained.

[0045] The hydrolyzable chloride in this fraction was analyzed by the method described above and found to be 29 ppm. The value of 2-chloro-2-methylpropionic acid 2-isocyanatoethyl ester analyzed by gas chromatography equipped with a flame ionization detector was 265 ppm in terms of the ratio of peak area of the compound to the entire peak area derived from the sample (hereinafter referred to a "simple peak area ratio") on the chromatogram.

[0046] Thereafter, two glass columns each having an inner diameter of 20 mm and a length of 30 cm and packed with 3 mmϕ Dixon packing were connected in series and by using this as the rectification tower, 150 g of the purified 2-isocyanatoethyl methacrylate obtained above having added thereto 0.15 g of phenothiazine was distilled at about 0.7 kPa, a distillation temperature of 70°C and a bottom temperature of 81°C.

[0047] When an initial fraction of 14.8 g was distilled, the receiver was changed and continuously, 53 g was distilled. This fraction was analyzed by gas chromatography but 2-chloro-2-methylpropionic acid 2-isocyanatoethyl ester was not detected. Also, the hydrolyzable chloride content was analyzed and found to be nil (detection limit: 1 ppm or less).

Comparative Example 1

[0048] The 2-isocyanatoethyl methacrylate containing 381 ppm of hydrolyzable chloride used in Example 1 was distilled in the same manner using the distillation equipment of Example 1 except for omitting the pre-treatment. When an initial fraction of 15 g was distilled, the receiver was changed and continuously 51 g was distilled. In the fraction obtained, 2-chloro-2-methylpropionic acid 2-isocyanatoethyl ester was not detected but hydrolyzable chloride content analyzed was found to be 124 ppm.

Comparative Example 2

[0049] The procedure of Example 1 was repeated except that one glass column of Example 1 was used as the distillation tower and the packing was changed to 6 mmϕ Dixon packing.

[0050] In the distillate obtained, 0.01% in terms of a simple peak area ratio of 2-chloro-2-methylpropionic acid 2-isocyanatoethyl ester was detected and the hydrolyzable chloride content analyzed was found to be 16 ppm.

Example 2

[0051] The procedure of Example 1 was repeated except for using 2-isocyanatoethyl acrylate having a hydrolyzable chloride content of 460 ppm.

[0052] The distillate obtained was analyzed by gas chromatography but 2-chloropropionic acid 2-isocyanatoethyl ester was not detected. Further, the hydrolyzable chloride was found to be below the detection limit.

Example 3

[0053] The procedure of Example 1 was repeated except for using 2-isocyanatopropyl methacrylate having a hydrolyzable chloride content of 451 ppm. The distillate obtained was analyzed by gas chromatography but 2-chloro-2-methylpropionic acid 2-isocyanatopropyl ester was not detected. Further, the hydrolyzable chloride content was found to be below the detection limit.

[0054] According to the present invention, an isocyanatoalkyl (meth)acrylate substantially free of hydrolyzable chloride can be industrially produced. In particular, the isocyanatoalkyl (meth)acrylate produced can be used as a raw material of an active radiation curable resin or the like suitable for uses having a dislike to chlorine, such as electronic materials.

Claims

1. A method for producing an isocyanatoalkyl (meth)acrylate substantially free of hydrolyzable chloride, comprising

   purifying an isocyanatoalkyl (meth)acrylate containing hydrolyzable chloride until in case of an isocyanatoalkyl acrylate a 2-chloropropionic acid isocyanatoalkyl ester or in case of an isocyanatoalkyl methacrylate a 2-methyl-2-chloropropionic acid isocyanatoalkyl ester is substantially eliminated.

2. The production method as claimed in claim 1, wherein the isocyanatoalkyl (meth)acrylate used in the purification step has a hydrolyzable chloride content of 100 ppm or less.

3. The production method as claimed in claim 2, wherein the isocyanatoalkyl (meth)acrylate containing a hydrolyzable chloride is treated with an epoxy group-containing compound and an amine and/or an imidazole to reduce the content of the hydrolyzable chloride in the isocyanatoalkyl (meth)acrylate to 100 ppm or less, and then further purified.

4. The production method as claimed in any one of claims 1 to 3, wherein the purification comprises distilling at a distillation temperature of less than 100°C under reduced pressure in the presence of a polymerization inhibitor.

5. The production method as claimed in claim 3 or 4, wherein the amine is a trialkylamine with the alkyl moiety having from 4 to 15 carbon atoms or a compound represented by the following formula (I)

$$H_2N\text{-}(CH_2CH_2NH)_n\text{-}H \qquad (I)$$

   wherein n represents an integer of 2 or more; and the imidazole is a 2-alkyl-4-alkylimidazole with the alkyl groups each independently having from 1 to 3 carbon atoms.

6. The production method as claimed in any one of claims 3 to 5, wherein the treating is performed using an epoxy group-containing compound in an amount of from 1 to 10 molar times and an amine and/or an imidazole in an amount of from 0.2 to 2 molar times the content of the hydrolyzable chloride.

7. The production method as claimed in any one of claims 1 to 6, wherein the isocyanatoalkyl (meth)acrylate is 2-isocyanatoethyl methacrylate.

8. An isocyanatoalkyl (meth)acrylate substantially free of hydrolyzable chloride, comprising an isocyanatoalkyl acrylate containing substantially no 2-chloropropionic acid isocyanatoalkyl ester or an isocyanatoalkyl methacrylate containing substantially no 2-methyl-2-chloropropionic acid isocyanatoalkyl ester.

9. 2-isocyanatoethyl methacrylate substantially free of hydrolyzable chloride, which contains substantially no 2-methyl-2-chloropropionic acid 2-isocyanatoethyl ester.

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(54) Method for producing isocyanatoalkyl (meth)acrylate

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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	31 May 1999	HOFBAUER

CATEGORY OF CITED DOCUMENTS

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